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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C01B 31/02 A1

(11) International Publication Number: WO 93/19007

(43) International Publication Date: 30 September 1993 (30.09.93)

(21) International Application Number: PCT/US92/07491

(22) International Filing Date: 4 September 1992 (04.09.92)

(30) Priority data:
855,802 18 March 1992 (18.03.92) US

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(81) Designated State: JP.

Published
With international search report.

(54) Title: METASTABLE FULLERENES

(57) Abstract

Metastable fullerenes have been identified and isolated, in particular, the metastable fullerenes are isomers of the stable forms of C_{60} and C_{70} fullerenes. Metastable fullerenes convert to a fullerene of the same molecular weight upon heating. A fulleren isomer is isolated and identified. The fullerene isomer has the M_+ and M^{+2} ions identical to that of a fullerene having a formula C_x, where x is in the range of 60 to 75 and further having a retention time in liquid chromatography differing from that of the fullerene having the formula C_x.

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Metastable Fullerenes

Cross-Reference to Related Patents

The present application is a continuation-in-part application of copending application U.S.S.N. 07/605,310, filed May 24, 1991.

Field of the Invention

The present invention relates to closed-caged carbon molecules known as Buckminsterfullerenes or fullerenes and isomers thereof.

Background of the Invention

Fullerenes were first reported by Kroto *et al.* in carbon vapor produced by laser irradiation of graphite ((*Nature* **318**, 162-164 (1985)). Fullerene C_{60} is a closed cage carbon structure containing 20 six-membered rings and 12 five-membered rings with the appearance of a soccer ball. There has been a surge of scientific interest in these compounds because they represent a new class of carbon in addition to the two known forms, graphite and diamond.

Fullerenes have many potential applications. The ability to intercalate metal cations into the structure suggests uses as catalysts in industrial processes. The potassium-fullerene C_{60} is a superconductor with a T_c of 11 K. The fullerene C_{60} surface is susceptible to chemical reactions such a hydrogenation and fluorination. Fluorinated fullerenes are expected to be good lubricants. Extensive research is being conducted throughout the United states and the world to develop or discover new and useful fullerenes.

Diederich *et al.* (*Science* **254**, 1768-1770(1991) reported the isolation and characterization of isomeric C_{78} fullerenes. However, isomeric forms of lower fullerenes are unknown, in particular, C_x, where x is less than 78.

Summary of the Invention

In the parent application of which this is a continuation-in-part it is disclosed that fullerenes could be produced in flames.

In one aspect of the present invention, the applicants have recognized that, in addition to the fullerenes reported in the parent application, sizable quantities of a metastable fullerene can also be present. By "metastable", as that term is used herein, it is meant a species that is transient but of sufficient stability to permit isolation under specific conditions. In preferred embodiments of the invention, the molecular formula of the metastable fullerene is C_{60}. In other preferred embodiments, the molecular formula of the metastable fullerene is C_{70}. The metastable fullerene converts to a fullerene having the same molecular formula upon heating. The "isolated pentagon rule" requires that no two pentagonal carbon sub-units of closed-cage structure lie adjacent to one another. Metastability may be the result of having adjacent pentagonal carbon sub-units in the isomeric fullerene.

In another aspect of the invention, a fullerene isomer is provided having M^+ and M^{+2} ions identical to that of a stable fullerene and further having a retention time in liquid chromatography differing from that of the fullerene having the formula C_x. By "M^+ and M^{+2} ions", as that term is used herein, it is meant the singly and doubly charged parent ion peaks identified upon mass spectroscopic analysis. By "isomer", as that term is used herein, it is meant a structural or conformational variation of a compound having the same molecular formula as the known fullerenes. Isomers of C_{60}, C_{70}, C_{76}, C_{84}, C_{90} and C_{94} have been isolated and characterized. However, it is recognized that isomers of other fullerenes, particularly of higher molecular weight, are produced.

In a preferred embodiment of the invention, the fullerene isomer is metastable. Isomers of fullerene C_{60} were considered to be unlikely in view of the fact that the known "soccer ball" structure which possesses 12 five-membered or

pentagonal rings completely surrounded by the 20 six-membered or hexagonal rings is the only possible arrangement which obeys the "isolated pentagon rule".

In another aspect of the invention, the yield of a metastable isomer can be optimized in any fullerene source by rapidly quenching the fullerenes at a location in the process where the fullerenes are being produced. In a preferred embodiment, metastable isomer yield is improved by avoiding high temperatures in post-production treatments. The metastable fullerene converts readily under the high temperature conditions of the flame. By quenching the reaction before there is sufficient time to allow the complete conversion of the metastable to the stable fullerene, the yield of metastable fullerene is enhanced. Likewise, means taken to avoid subjecting the metastable compound to conditions that would encourage conversion to the more stable form of the fullerene during isolation and purification will enhance the final yield of metastable fullerene. Means of quenching include, but are not limited to, inserting a collection tube near the location of fullerene formation into which is introduced the cold nitrogen evaporant from liquid nitrogen source or by injecting a fluid from high velocity jets into the location of fullerene production.

Analysis of materials made by the process disclosed in the parent application indicate the presence of isomers of C_{60} and C_{70} fullerenes. In the purification of soot samples by high performance liquid chromatography (HPLC), species were observed with retention times differing from those of the C_{60} and C_{70} fullerenes. Mass spectrometer analysis of the different species indicated that they had the same mass as the known C_{60} and C_{70} fullerenes. It is speculated that the isomer of the C_{60} fullerene may have a flattened, pillow-like configuration, a cylindrical structure or even a flattened cylindrical structure. It has also been determined that the isomers are metastable and will revert to the respective fullerene under appropriate conditions. Because of their metastable nature and because of their different structure, these isomers may be more useful than the base fullerene for certain application. For example, the metastable isomer may be more easily

doped with atoms such as potassium for making a known superconducting fullerene. Another potential application of the metastable isomer is as a starting material for making diamonds using the application of extremely high pressures, for example, diamond anvils. These meta stable fullerenes may be useful as starting materials for chemical addition or polymerization reactions.

Brief Description of the Drawing

In the Drawing:

Figure 1 is a high performance liquid chromatogram (HPLC) of a toluene extract of a flame soot indicating C_{60} and C_{70} as well as new peaks A-D;

Figure 2 is selected ion chromatograms (SIC) from the HPLC-MS analysis of a flame soot;

Figure 3 is a background-subtracted positive mass spectra obtained at the crests of chromatographic peaks annotated in Figure 2;

Figure 4 is a background-subtracted negative ion mass spectra obtained at the crests of chromatographic peaks annotated in Figure 2; and

Figure 5 illustrates the time-dependence of chromatographic peak areas from HPLC analysis of flame-derived fullerene extract in boiling toluene under argon.

Description of the Preferred Embodiment

The structure of the remarkably stable carbon cluster C_{60}, first discovered by Kroto *et al.* (*Nature* **318**, 162 (1985)) in vapor from laser irradiation of graphite and subsequently produced in macroscopic quantities by resistive heating of graphite under an inert atmosphere (Krätschmer *et al.*, *Nature* **347**, 354 (1990); Taylor *et al.*, *JCS Chem. Commun.* 1423 (1990); Ajie *et al.*, *J. Phys. Chem.* **94**, 8630 (1990); Haufler *et al.*, *J. Phys. Chem.* **94**, 8634-8636 (1990)), is now widely accepted as a truncated icosahedron ("soccer ball fullerene"), while the homologue C_{70} is assigned an ellipsoidal cage structure ("rugby ball", Stoddart, *Angew. Chem. Int. Ed. Engl.* **30**, 70-72 (1991)).

"Buckminsterfullerene" and "fullerene" as these terms are used herein refer to these highly symmetrical closed-cage carbon clusters. The parent application discloses that C_{60} and C_{70} fullerenes, isolated from samples of condensible compounds and soot collected from controlled combustion of benzene in pre-mixed laminar flames, were spectroscopically indistinguishable from fullerenes prepared from graphite. Analysis of the flame samples by high-performance liquid chromatography (HPLC) with ultraviolet spectroscopic detection (UVD) also revealed the presence of several additional components with fullerene-like characteristics.

Efficient methods for the analysis of polycyclic aromatic compounds (PACs) of high molecular weight, by HPLC or supercritical fluid chromatography (SFC) coupled directly to mass spectrometry (LC-MS or SFC-MS), have been developed recently. These methods employ either a moving-belt interface with flash heating of the analyte as it enters the EI source, or a heated pneumatic nebulizer coupled to an atmospheric pressure chemical ionization (APCI) source in which electron transfer to benzene molecular cations is arranged to be the dominant ionization mechanism. In the present work the flame soot samples were analyzed by these complementary LC-MS techniques, as well as by HPLC interfaced on-line to a diode array detector for UV spectroscopy.

<u>Experimental.</u>

Materials. The extracts of flame-generated soots and condensates were identical to those described in the parent application. A sample of soot produced by resistive heating of graphite, and one of a purified extract of C_{60} from such soot (containing also a few per cent of the C_{70} fullerene), were obtained from the Texas Fullerenes Corpn., Houston, Texas 77030.

HPLC with UV spectroscopy. The column used was 25cm long x 2.1 mm i.d., with Vydac 201TP C_{18} packing. The initial solvent was 100% acetonitrile for 5 min, then programmed linearly to 100% dichloromethane over 45 min, held for 5 min, then programmed back to initial composition over 5 min. The mobile phase flow rate was 200 µL/min, with an injection volume of 5 µL. A HP1090M liquid chromatograph (Hewlett Packard

Co.,Palo Alto, CA, USA), equipped with a binary DR5 solvent delivery system, a HP1040A diode array detector, and a HP7994A data system, was used in all LC-UV analyses. The detector was configured for continuous full UV scan acquisition (220-600 nm).

HPLC with on-line mass spectrometry. The HPLC conditions were identical to those used in the LC-UV analyses. In one set of experiments the HPLC effluent (no split) was introduced to an electron ionization mass spectrometer (VG 20-250 quadrupole mass filter, VG Mass Lab, Altrincham, U.K.) *via* a VG moving belt interface. The conditions used were similar to those for LC-MS analysis of PACs with molecular weights of up to 600, except that the fullerenes and related compounds required higher temperatures for efficient volatilization. The nominal electron energy was 70 eV, with a trap current of 100 µA. The source temperature was 350°C, and the flash belt heater at the tip of the belt interface, located within the body of the ion source, was operated at maximum power (belt surface temperature unknown). In addition, the belt clean-up heater (also at maximum power) and wash-bath had to be employed in order to avoid memory effects. A VG 11-250J data system was used for instrument control and for data acquisition and processing.

The LC-MS experiments employing electron transfer APCI were conducted using an API III triple quadrupole instrument (SCIEX, Thornhill, Ontario), equipped with a heated pneumatic nebuliser interface (SCIEX). The pneumatic nebuliser is contained within a concentric quartz heating tube, itself located within the room temperature APCI source; the indicating thermocouple is located on the exterior surface of this heating tube, together with the heating element. Experiments conducted on this nebuliser interface mounted on the bench but under conditions otherwise identical to those used in the LC-MS analyses, with a second thermocouple used to probe the gas temperatures within the interface, showed that the maximum temperatures experienced by the analytes under these conditions fell in the range 80-100°C. Medical quality air was normally used as the nebulizing gas, but was replaced by high-purity nitrogen for a few experiments; high purity nitrogen

was always used for the counter-current gas flow (the "gas curtain") which prevents unevaporated droplets and other debris from clogging the orifice connecting the API chamber to the mass spectrometer vacuum system.

Ionization was achieved in a fashion very similar to that described for SFC-MS analysis of PACs. The APCI plasma was sustained by a cold corona discharge (stainless steel needle maintained at 3 kV). Introduction of benzene vapor *via* the nebulizing gas inlet ensured that the dominant positive reactant ions in the plasma were $C_6H_6^{+\cdot}$, together with some water cluster ions from residual water in the system. Under these conditions the predominant ionization mechanism for polycyclic aromatic hydrocarbons (PAHs) involves electron transfer to $C_6H_6^{+\cdot}$, with some tendency for protonation. Characterization of this APCI plasma in the absence of analytes also showed a significant population of benzene-derived ions at m/z 91, presumably $C_7H_7^+$ ions of tropylium structure.

Results and Discussion.

Identification of Peaks I and II as closed-cage fullerenes. The LC-UV analysis of the flame-soot extract (Fig. 1) was compared to that of an extract of soot produced by resistive heating of graphite. This comparison permitted identification of peaks I and II in Fig. 1 as C_{60} and C_{70} fullerenes, *via* both retention times and UV spectra. Further confirmation was obtained by HPLC-MS experiments using a moving-belt interface and an EI source. The reconstructed total ion chromatogram (not shown) matched Fig. 1 extremely well, although some of the smaller HPLC peaks were not well defined. The EI mass spectra (not shown) recorded at the crests of peaks I and II (Fig. 1) were identical to those for C_{60} and C0d.

Identification of Peaks B and C as C_{60} and C_{70} species. Peaks B and C in Fig. 1 were of particular interest since they were absent from the chromatogram of extract of soot from resistive heating of graphite. As shown in Fig. 1 the UV spectra obtained at the crests of Peaks B and C differ from those of the authentic C_{60} and C_{70} fullerenes (Peaks I and II), but do have fullerene-like characteristics. Surprisingly, the EI mass spectra acquired in

the moving-belt LC-MS experiments at the crests of peaks B and C were identical to those for peaks I and II respectively, showing intense $M^{+\cdot}$ and M^{2+} ions with appropriate isotopic distributions. This combined UV and EI evidence strongly suggested that peaks B and C arose from isomers of the C_{60} and C_{70} fullerenes.

However, at least two other interpretations of these HPLC-MS experiments are possible, based on the hypothesis that the additional abundant components in the flame soot extract (peaks B and C) were adducts (*e.g.* with oxygen) of the C_{60} and C_{70} fullerenes. Such compounds could conceivably yield negligible intensities of molecular ions upon electron ionization, but abundant fragment ions $C_{60}^{+\cdot}$ and $C_{70}^{+\cdot}$. However, the intense dications C_{60}^{2+} and C_{70}^{2+} are more difficult to rationalize on this basis. Alternatively, thermal decomposition of labile fullerene adducts to the parent compounds, subsequent to chromatographic separation and during the volatilization from the moving belt (several hundreds of °C at the belt-tip heater inside the ion source) *prior* to ionization, could not be excluded.

This hypothesis of labile fullerene adducts, which survived the chromatography but decomposed either before or after EI, was tested *via* treatment of each of the soot extracts (generated in flames or by resistive heating of graphite) with ferrous ammonium sulphate, and separately with sodium borohydride, in order to reduce suspected oxygen adducts. In other experiments the extracts were treated by passage through an activated alumina column in order to remove any hydroperoxides. All three treatments left the chromatogram (Fig. 1) unchanged. However, refluxing the extracts in boiling toluene (111°C) under argon resulted in a slow loss (half-life approximately 1 hour) of peaks B and C, with corresponding increases in peaks I and II whose UV spectra were thereby unchanged. A systematic study of the time dependence of these thermal transformations was undertaken, but this is best described below, after discussion of the confirmation of the identities of the HPLC peaks.

Clearly, a gentler and more sensitive method of HPLC-MS coupling was required. This was achieved using an APCI source, similar to that used

for SFC-MS analyses of PACs. The HPLC effluent was nebulized to micron-sized droplets within a heated quartz tube; the maximum gas temperature in this region was about 110°C in the first experiments, later reduced to 80-90°C with no significant change in the results obtained. The mobile phase was rapidly evaporated from these droplets *via* interactions with the heated gas (nitrogen saturated with benzene vapor, together with vaporized mobile phase), leaving extremely small particles each containing only a few analyte molecules. The vapor pressure of such small particles can be many times larger than that of the bulk material, permitting vaporization of analytes which are thermally labile when heated in the bulk phase. The vaporized sample was then drifted into a cold corona-discharge plasma, whose composition was controlled by manipulating that of the atmosphere in the APCI source. In this work post-column addition of benzene ensured that the dominant mechanism for formation of positive ions from the sample was electron transfer to $C_6H_6^{+\cdot}$ ions, whose recombination energy is 9.25 eV. Since the ionization energy of $C_{60}(g)$ is about 7.8 eV, electron transfer ionization was efficient and the excess energy of 1.5 eV was readily degraded by collisions with the atmosphere. A minor ionization mechanism was formation of adducts with tropylium ions ($C_7H_7^+$, m/z 91) formed from benzene in the APCI plasma. The sample-derived ions thus transmitted to the mass analyzer were internally cold, yielding mass spectra which exhibit only molecular and adduct ions with little or no fragmentation.

Results obtained by such HPLC-MS analysis of the flame sample are summarized in Fig. 2 and 3. The selected ion chromatogram (SIC) for $C_{60}^{+\cdot}$ at m/z 720 (Fig. 2a) shows two peaks at retention times matching those of peaks B and I (Fig. 1). The APCI mass spectra recorded at these two peak crests were identical to one another (Fig. 3a), dominated by molecular ions $C_{60}^{+\cdot}$ although the isotopic intensity distributions indicate a minor contribution from $C_{60}H^+$ formed by proton transfer from residual water cluster ions. Corresponding data acquired for the extract of the graphite soot (not shown) gave an identical spectrum for peak I (C_{60} fullerene). Analogous results obtained for peaks C and II (Fig.s 2c and 3b) suggest that peak C is

a C_{70} isomer and that other C_{70} isomers are present at lower abundances.

The short contact times (< 5 sec) and low temperatures (100°C and 80-90°C) experienced by the analytes in the APCI interface, compared with those in the refluxing toluene experiments, make it improbable that peaks A and B correspond to thermally labile adducts of the fullerenes which survived the chromatography but decomposed to C_{60} and C_{70} in the heated nebuliser. This conclusion was verified by flow-injection of an aliquot of the flame soot extract through the heated nebuliser, using the same mobile phase and thermal settings as for the HPLC-MS experiments but physically removed from the mass spectrometer and corona discharge. The emerging vapor was condensed on a cold surface, redissolved, and analyzed. All of peaks A-D survived this treatment, confirming the stability of the sample under these HPLC-MS conditions prior to ionization.

It is difficult to produce equally convincing evidence to contradict the hypothesis of fullerene adducts which survive *both* the chromatography *and* vaporization in the heated nebuliser interface, but whose molecular ions undergo facile and complete fragmentation to $C_{60}^{+\cdot}$ and $C_{70}^{+\cdot}$. However, in our hands this ionization method invariably produces abundant molecular ions, with no fragmentation, from fragile and relatively involatile analytes of a wide variety of structural types. In addition the evidence for formation of $(C_{60}+H)^+$ and $(C_{60}+C_7H_7)^+$ ions, and analogous adduct ions from C_{70} (Fig.s 3a and 3b), support the contention that peaks B and C correspond to C_{60} and C_{70} species, respectively. Further support of this interpretation is provided by negative ion APCI spectra (Fig. 4), obtained under LC-MS conditions identical to those used for the positive ion work (Fig.s 2 and 3) but omitting the benzene. Under these conditions, ionization of the C_{60} and C_{70} compounds proceeds *via* two principal mechanisms, *viz.* electron attachment and chloride attachment (the Cl^- arising from the dichloromethane in the HPLC mobile phase). As shown in Fig. 4 the spectrum obtained for Peak B is almost identical to that for Peak I (the authentic C_{60} fullerene), further supporting the present contention that Peak B corresponds to a chromatographically distinguishable form of C_{60} rather than to some adduct of C_{60} which,

subsequent to ionization, fragments immediately to yield a mass spectrum which is identical to that formed directly from ionization of the authentic fullerene. Slight differences between the two spectra in Fig. 4 are due mostly to differences between the compositions of the APCI plasma in the two cases, under the HPLC gradient conditions used in these LC-MS experiments. Detailed interpretation of these negative ion spectra will be published separately, but it is noted here that contributions to the spectra include those from less important ionization mechanisms involving oxygen anions derived from the nebulizing gas (usually air) and from residual water. Finally, a comparison of the analogous negative ion spectra (not shown), obtained for Peaks C and II, similarly supported the proposal that both peaks correspond to C_{70} species.

The evidence supports the contention that Peaks B and C, in the HPLC chromatograms of the flame-generated fullerenes[8], arise from *isomers* of the C_{60} and C_{70} fullerenes, respectively.

Identification of other HPLC peaks as higher carbon clusters or monoxides. Higher carbon clusters were also observed at lower abundances in the flame-generated extracts. Thus, peak D (Fig. 1) corresponds to C_{84} (Fig. 2f). The two minor non-annotated peaks preceding Peak D (Fig. 1) correspond to C_{76} (Fig.s 2e and 3c); a chiral form of C_{76} was isolated and characterized very recently by Diederich *et al.* Evidence was also obtained (not shown) for several forms of C_{90} and C_{94}, present at very low abundances in this extract. Note that the mass spectra obtained for these minor components, *e.g.* Fig. 3c, were obtained near the ion statistical limit so that significant random deviations of the isotope intensity distributions, from those predicted from assumed molecular formulae, were observed.

Peak A (Fig. 1) was identified as a monoxide $C_{60}O$ *via* the APCI mass spectrum, which showed evidence for increased importance of protonation to form $(M + H)^+$ (Fig. 3d) relative to that of the C_{60} compounds. The SIC for m/z 736 (Fig. 2b) shows evidence for at least 5 chromatographically distinguishable species giving rise to $C_{60}O^{+\cdot}$, but two of these have retention times identical to those of peaks B and I and were probably formed as

oxidation artifacts of the corresponding carbon clusters in the APCI plasma. This was confirmed by repeating the analysis with meticulous exclusion of air (using high purity nitrogen as nebulizing gas) and of water, insofar as this was possible; as a result the intensities of the oxidation artifacts were reduced by a factor of about 5, while those of the chromatographically distinguishable monoxides remained unaffected. Analysis of the graphite soot gave an SIC for m/z 736 (not shown) containing only peak A plus a weak APCI artifact corresponding to Peak I. These observations are susceptible to an interpretation in which Peak A is the unique monoxide of C_{60} buckminsterfullerene (all carbons equivalent), while the other non-artifact signals in Fig. 2b correspond to monoxides of less symmetrical C_{60} isomers not present in the graphite soot. Fig. 2d shows similar evidence for several $C_{70}O$ isomers in the flame soot, apart from the APCI artifacts. The corresponding experiment on the graphite soot extract (not shown) showed evidence for only two $C_{70}O$ compounds apart from the APCI artifact at a retention time corresponding to Peak II; this observation is again qualitatively consistent with the requirement that the new C_{70} isomers (Fig. 2c) possess a lower degree of molecular symmetry than does the authentic fullerene. One $C_{70}O$ compound has been isolated previously[14] from a soot produced by resistive heating of graphite.

All of these findings summarized in Fig.s 2 and 3 were qualitatively confirmed by repeating the HPLC-MS analyses in negative ion mode. The observed multiplicities of the $C_{60}O$ and $C_{70}O$ isomers provide circumstantial evidence supporting the conclusion, described above, that Peaks B and C correspond to isomers of the C_{60} and C_{70} fullerenes with lower degrees of molecular symmetry.

Rates of thermal conversion of C_{60} and C_{70} isomers to stable fullerenes. The lower stabilities of the newly observed isomers, relative to those of the respective previously observed fullerene structures, is qualitatively consistent with calculated relative stabilities by Schmalz *et al.* (*J. Am. Chem. Soc.* **110**, 1113 (1988)) and with more recent predictions by Goeres and Sedimayr (*Chem. Phys. Lett.* **184**, 310 (1991)) based upon a theoretical nucleation

mechanism for formation of fullerenes.

In the present work, the rate of thermal conversion of the new isomers to their fullerene counterparts was studied in solution in deaerated boiling toluene (111°C), in an argon atmosphere. A few LC-MS experiments, using the positive ion APCI method, were run to confirm the identities of reactants and products of the thermolysis process, but the quantitative data were obtained using LC-UV analyses similar to that illustrated in Fig. 1. In all cases coronene was added to the extract solution as a non-reactive internal standard, to avoid concentration errors due to evaporation of solvent. Several experiments were run in parallel, with quenching at varying reaction times. The results thus obtained are illustrated in Fig. 5, for the C_{60} species only (similar results were obtained for the C_{70} species). The peak areas plotted in Fig. 5 are for appropriate HPLC peaks annotated in Fig. 1, monitored *via* the integrated optical absorptions over the range 260-340 nm; thus, no correction was possible for differences in molar extinction coefficients.

The decay of Peak B (new C_{60} isomer) is observed to occur with a half-life of approximately 1 hour. The corresponding rise of Peak I (authentic C_{60} fullerene) does not compensate for the loss of Peak B intensity, as is most readily seen from the plot (Fig. 5) of the sum of the two intensities as a function of time. This could be due in part to a higher integrated molar absorption for the new isomer (Peak B) than for its fullerene counterpart, or to possible side-reactions. A small but significant rise (Fig. 5) in the intensity of Peak A ($C_{60}O$) suggests that some degree of oxidation occurred despite the precautions taken. Also, other processes such as polymerization would have yielded side-products which would not have been detected in these experiments.

What is claimed is:

1. A metastable fullerene.

2. The metastable fullerene of claim 1 wherein the structure of the fullerene includes at least one pair of adjacent pentagonal carbon units.

3. The metastable fullerene of claim 1 having the molecular formula of C_{60}.

4. The metastable fullerene of claim 1 having the molecular formula of C_{70}.

5. The metastable fullerene of claim 1 wherein the metastable fullerene is converted to a fullerene of same molecular formula upon heating.

6. A fullerene isomer, characterized by

a M^+ and M^{2+} ions by mass spectroscopy identical to that of a stable fullerene; and

a retention time in liquid chromatography differing from the retention time of the fullerene having a formula C_x.

7. A fullerene isomer, characterized by

a M^+ and M^{2+} ions by mass spectroscopy identical to that of a fullerene;

a retention time in liquid chromatography differing from the retention time of the fullerene; and

which has a structure includes at least one pair of adjacent pentagonal carbon units.

8. The fullerene isomer of claim 6, wherein the isomer is metastable.

9. The fullerene isomer of claim 6, the isomer being a structural isomer of the fullerene having a structure of C_x.

10. The fullerene isomer of claim 6, the isomer being a conformational isomer of the fullerene having a formula of C_x.

11. The fullerene isomer of claim 6 or 7 wherein the molecular formula is C_{60}.

12. The fullerene isomer of claim 6 or 7 wherein the molecular formula is C_{70}.

13. The fullerene isomer of claim 6 or 7 wherein the molecular formula is C_{76}.

14. The fullerene isomer of claim 6 or 7 wherein the molecular formula is C_{84}.

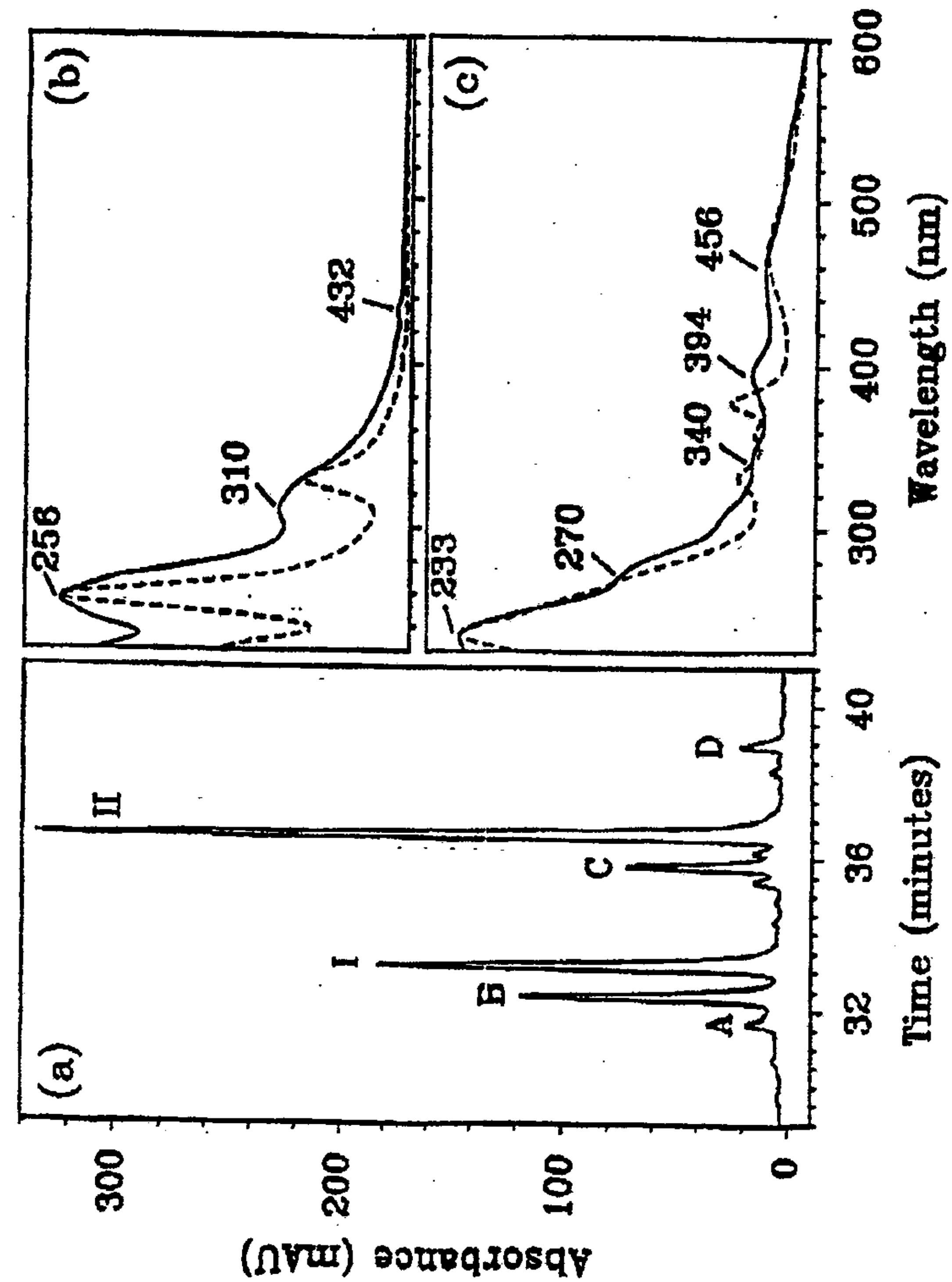
15. The fullerene isomer of claim 6 or 7 wherein the molecular formula is C_{90}.

16. The fullerene isomer of claim 6 or 7 wherein the molecula formula is C_{94}.

17. The fullerene isomer of claim 6, wherein the structure of the isomeric fullerene includes at least one pair of adjacent pentagonal carbon units.

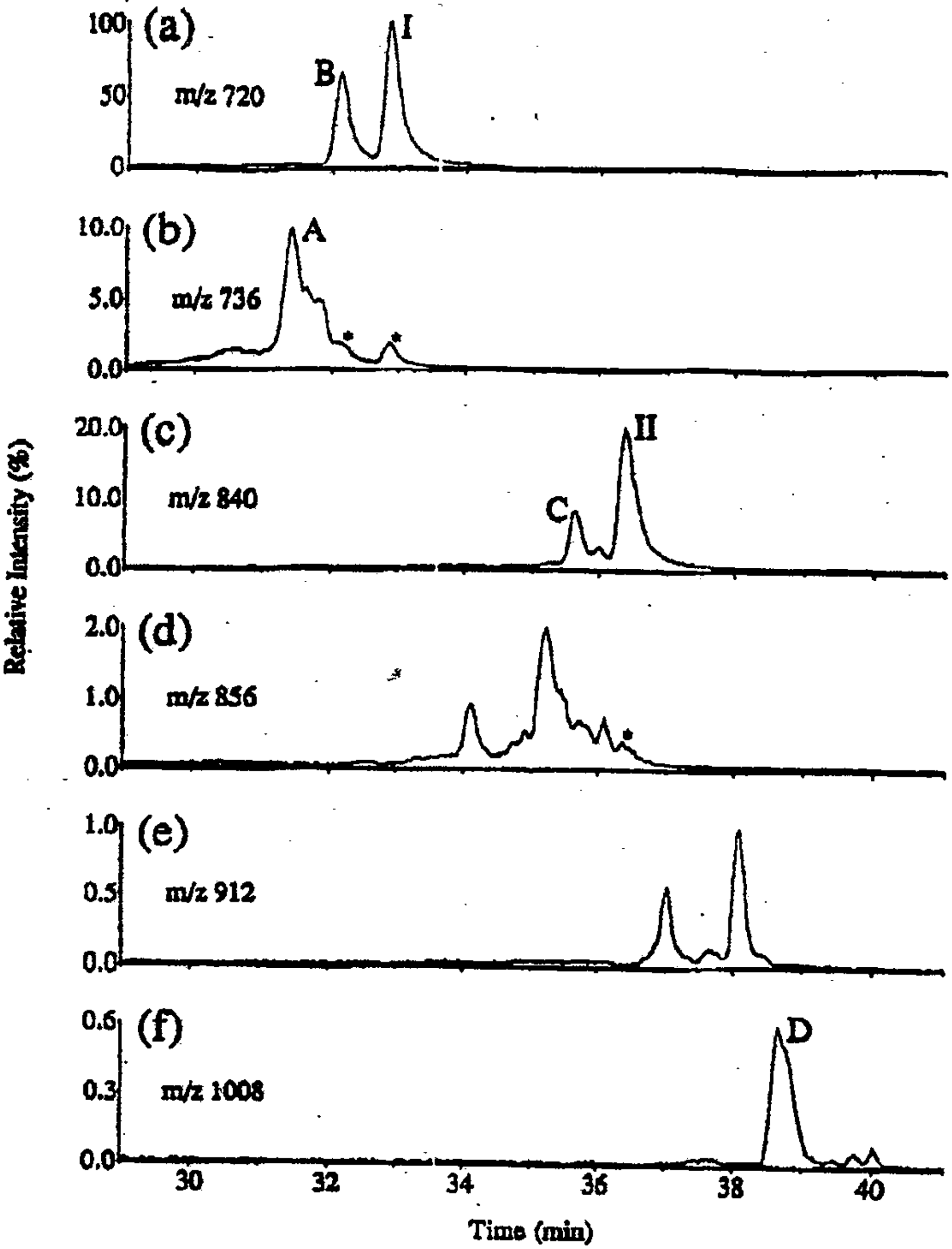
18. The method of optimizing the yield of a metastable fullerene isomer in a fullerene source, comprising increasing the quench rate of fullerenes at a point where fullerenes are being made.

19. The method of claim 18, further including avoiding high temperatures in a post-production treatment of a collected product.

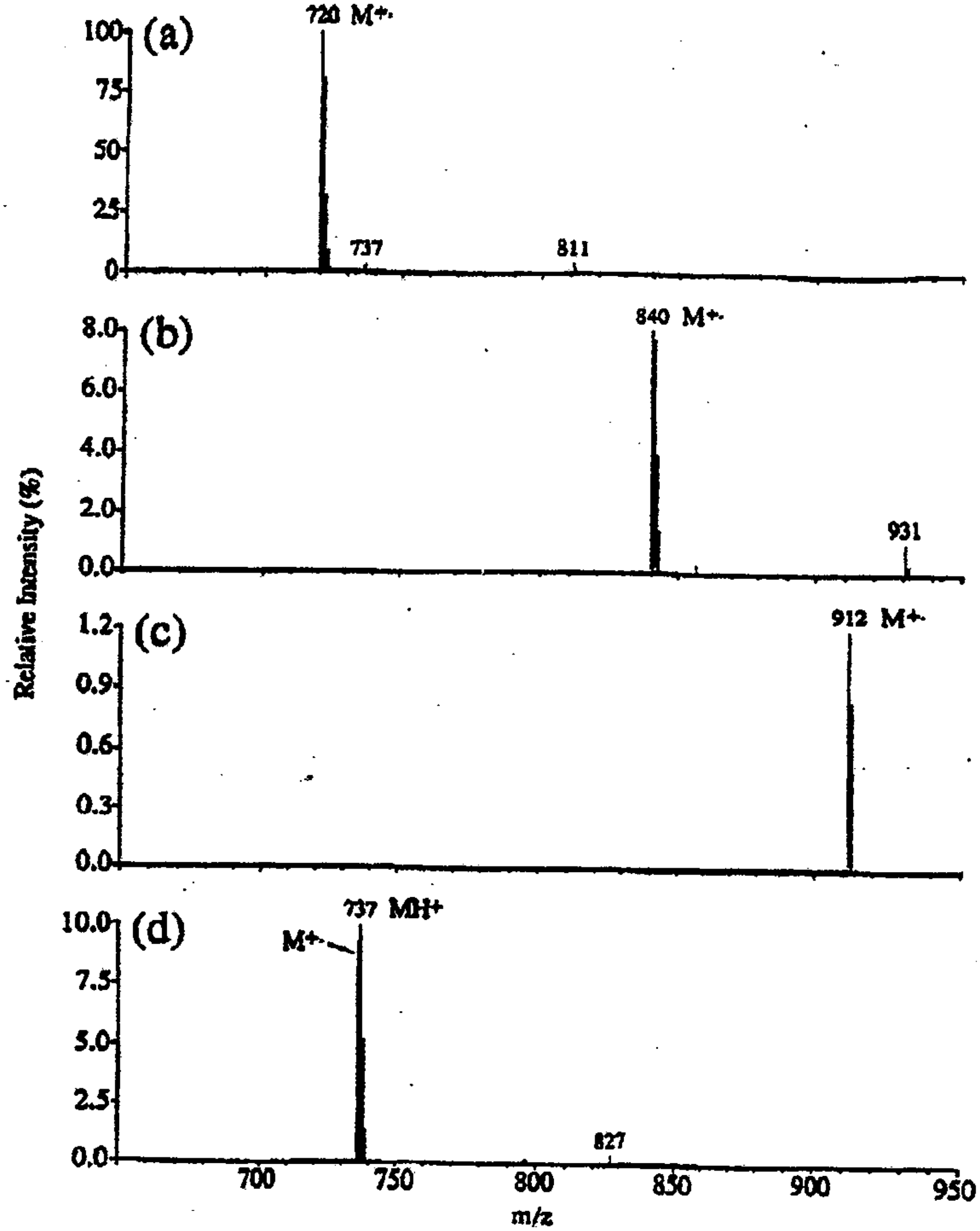


(a)
(b)
(c)
Absorbance (mAU)
300
200
100
0
A
B
I
C
II
D
32
36
40
Time (minutes)
256
310
432
233
270
340
394
456
300
400
500
600
Wavelength (nm)

Fig. 1



(a)
m/z 720
B
I
(b)
m/z 736
A
(c)
m/z 840
C
II
(d)
m/z 856
(e)
m/z 912
(f)
m/z 1008
D
Relative Intensity (%)
Time (min)



100
75
50
25
0
(a)
720 M+·
737
811
8.0
6.0
4.0
2.0
0.0
(b)
840 M+·
931
1.2
0.9
0.6
0.3
0.0
(c)
912 M+·
10.0
7.5
5.0
2.5
0.0
(d)
737 MH+
M+·
827
Relative Intensity (%)
700
750
800
850
900
950
m/z

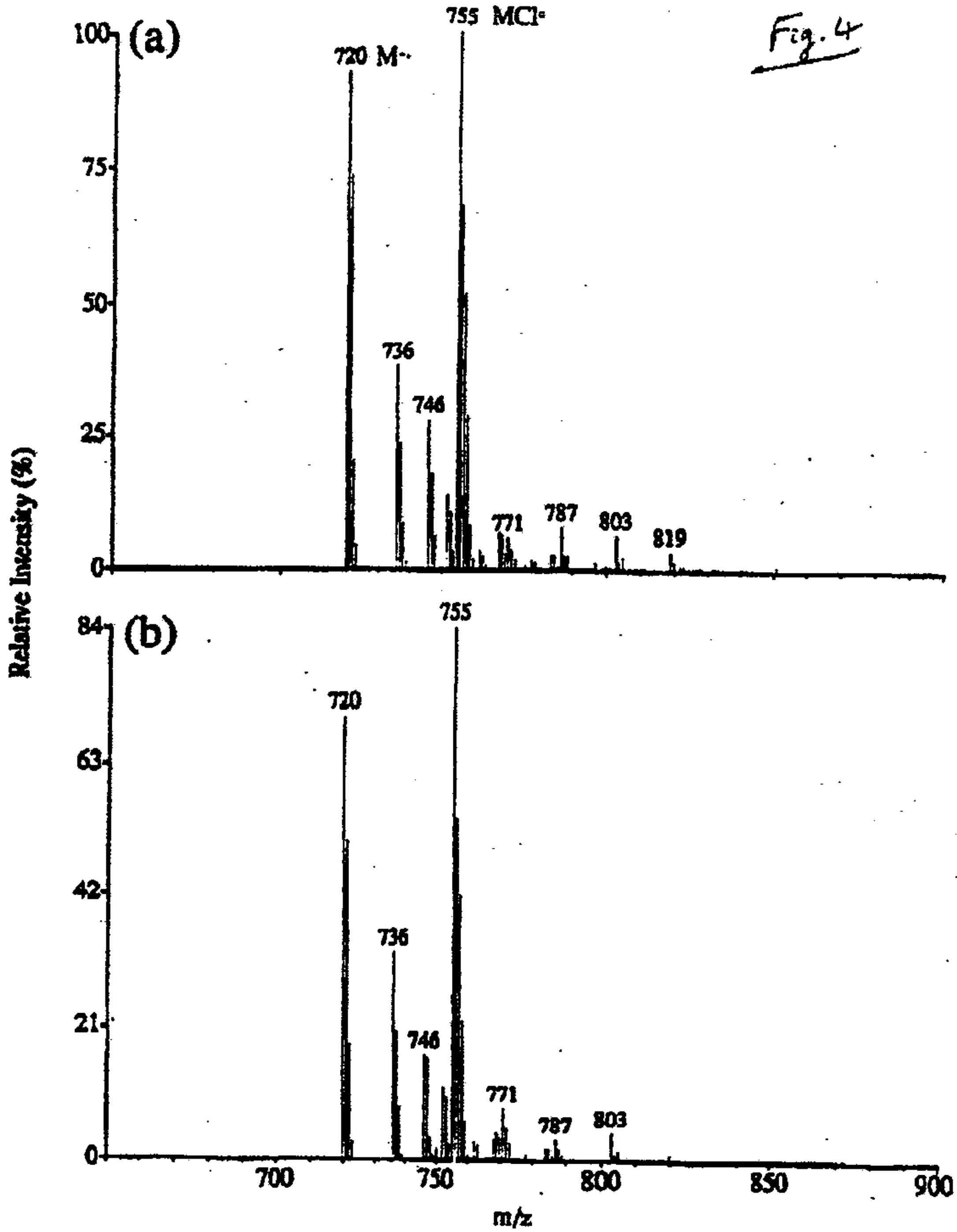
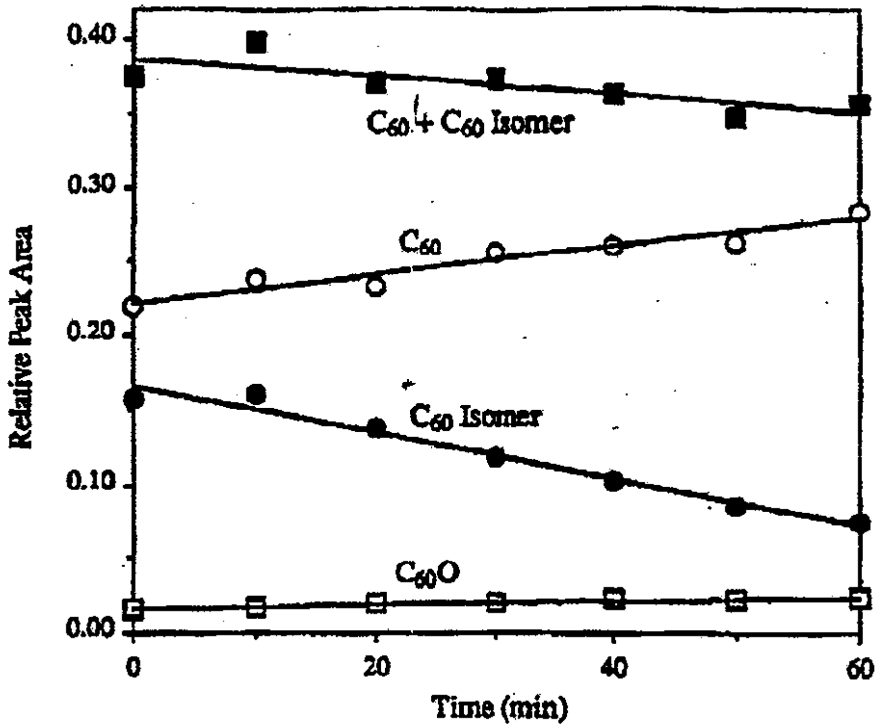


Fig. 4
(a)
720 M⁻·
755 MCl⁻
736
746
771
787
803
819
(b)
720
755
736
746
771
787
803
Relative Intensity (%)
m/z
0
25
50
75
100
21
42
63
84
700
750
800
850
900

Fig. 5


0.40
0.30
0.20
0.10
0.00
Relative Peak Area
C_{60} + C_{60} Isomer
C_{60}
C_{60} Isomer
$C_{60}O$
0
20
40
60
Time (min)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/07491

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5 C 01 B 31/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	C 01 B 31/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	Chemical Abstracts, vol. 115, no. 14, 7 October 1991, (Columbus, Ohio, US), C. COULOMBEAU et al.: "Study of 74 C60 carbon isomer aggregates by the Hueckel method", see page 435, abstract no. 142838w, & J. CHIM. PHYS. PHYS.-CHIM. BIOL. 1991, 88(5), 665-74 ---	
A	Chemical Abstracts, vol. 116, no. 8, 24 February 1992, (Columbus, Ohio, US), L. GOODWIN: "Structure and stability of some fullerene C60 isomers", see page 546, abstract no. 67712r, & PHYS. REV. B: CONDENS. MATTER 1991, 44(20), 11432-6 --- -/-	

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29-12-1992	18. 01. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	J. BREBION

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	Nature, vol. 352, 11 July 1991, (London, GB), J.B. HOWARd et al.: "Fullerenes C60 and C70 in flames", pages 139-141, see page 140, left-hand column, paragraph 1; figure 2 ---	
T	Chemical Physics Letters, vol. 184, no. 4, 27 September 1991, (Amsterdam, NL), A. GOERES et al.: "On the nucleation mechanism of effective fullerite condensation", pages 310-317 (cited in the application) ---	
T	Journal of the American Chemical Society, vol. 110, no. 4, 1988, (Washington, DC, US), T.G. SCHMALZ et al.: "Elemental carbon cages", pages 1113-1127 (cited in the application) ---	
P,X	Chemical Abstracts, vol. 117, no. 8, 24 August 1992, (Columbus, Ohio, US), J.B. HOWARD et al.: "Production of C60 and C70 fullerenes in benzene-oxygen flames", see page 856, abstract no. 82176h, & J. PHYS. CHEM. 1992, 96(16), 6657-62 -----	1,3,4